RAW MATERIALS

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USE OF NATURAL SODA FROM THE MIKHAILOVSKOE DEPOSIT IN THE PRODUCTION OF BUILDING GLASSES

N. S. Krasheninnikova,[1] I. V. Frolova,[1] O. V. Kaz'mina,[1] and V. I. Vereshchagin[1]

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A fundamental possibility of using natural soda for partial replacement of traditional soda-bearing materials in the production technology of sheet and other kinds of glasses is established. The physicochemical characteristics of natural soda and the specifics of its behavior at the stage of batch preparation by the granulation method are investigated, making it possible to identify optimum conditions for batch preparation.

The study of available material resources and the search for ways of their most effective application is critical for successful development of the industrial sector of construction materials, including glass materials.

One of problem confronted by the glass industry, in particular in West Siberia, is shortage of soda-bearing materials, primarily soda ash.

Current production of soda is based on four production methods: based on ammonia, nepheline, carbonization of sodium hydroxides, and natural soda.

The ammonia method is the most common in the world despite its serious disadvantages: a low degree of utilization of source material, not more than 30%, substantial quantities of waste generated, high energy consumption, and significant capital costs [1].

The above disadvantages, which used to be less significant than the advantages, are now becoming crucial. This is due to a growing need for complex utilization of natural materials, more strict environment-protection regulations, and increasing cost and shortage of power carriers. Therefore, one way of solving these problems consists in full or partial replacement of synthetic soda (SS) by more available, environmentally pure, and inexpensive alkali-bearing materials.

Russia has several deposits of natural soda on its territory: Petukhovskoe in the Omsk Region, Doroninskoe and Raichikhinskoe in the Khabarovsk Region, and Kiryanskoe in Buryatia; however, these soda lakes are currently not being exploited.

The Mikhailovskoe deposit in the Altai Region is of special interest for West Siberia. Mining of this deposit started in 1929. In different periods, soda was extracted by the basin method based on using soda resources in the surface brine of lakes; the mining method, when only soda ore from bottom deposits was used, and the filtration leaching method (1961 – 1976), which made it possible to process all types of soda resources, namely, in solid sediments and in surface and subsurface brine. Long-term practice demonstrated the high efficiency of this method for leaching soda-bearing rocks, even those with a poor soda content (below 1.5%).

In 1974 – 1988 this deposit was not operated due to the poor quality of soda obtained and its failure to compete with synthetic soda. While the deposit was exploited, processing technology was modified several times, which improved the quality of the product. However, the impurity content amounted to about 6% [2].

Due to changes in the economic situation of the country in recent years and urgent shortage it became expedient to operate the Mikhailovskoe deposit, which motivated setting up the Altai-Soda association in 1992, which resumed extraction of natural soda. Its resources converted to 100% sodium carbonate amount to over 3 million tons. The estimated period of working this deposit is about 70 years.

At present the Altai-Soda Association produces crystalline soda, which is a product of basin processing of solid bed deposits and subsurface soda brine using the methods of filtration leaching, concentration of brine in evaporating basins, and crystallization in sedimentary basins in the form of a strong layer extracted by soda-cutting machines.

According to chemical analysis data, raw soda from the Mikhailovskoe deposit contains (%) 27.49 Na_2CO_3, 5.30 Na_2SO_4, 2.11 NaCl, 62.7 H_2O, and 2.4 insoluble residue. The

[1] Tomsk Polytechnical University, Tomsk, Russia.

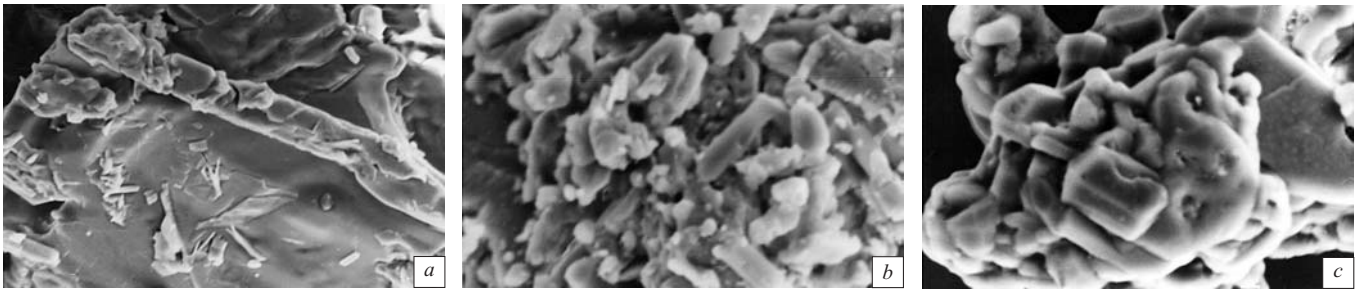

Fig. 1. Electron microscope photos (× 5000) of soda PS_1 (*a*), PS_2 (*b*), and synthetic soda (*c*).

main defect of raw soda is a 60% water content. Consequently, transportation, milling, and proportioning, of material presents serious difficulties.

The purpose of the present work was to study the composition and physicochemical properties of crystalline natural soda dried under different conditions:

– in a monolayer in air at temperature of 18 – 20°C (PS_1);
– in a muffle furnace at temperature of 350°C (PS_2)

For further investigation dried soda was milled in a disintegrator versus passing through a sieve with a cell size of 0.5 mm. The compositions of natural soda dried under different conditions and synthetic soda (Sterlitamak) determined by the chemical analysis methods in accordance with state standards are listed in Table 1.

The result of chemical analysis demonstrate a significant difference in the content of the main component (Na_2CO_3) in natural soda and synthetic soda. Natural soda contains small quantities of such compounds as SiO_2 and Al_2O_3, which are present in glass compositions and are not regarded as toxic impurities. Besides, soda from the Mikhailovskoe deposit has an increased content of Na_2SO_4 (18 – 20%) and Fe_2O_3 (0.11 – 0.13%). However, considering that natural soda is important for Siberia and other eastern regions of Russia, which do not have factories producing synthetic soda, the interest in this material is quite understandable.

The granulometric composition of soda was determined using the sieve analysis method. It was found that synthetic and natural soda PS_2 are mainly represented by fractions with particle size below 0.3 mm in the amount of 95 and 90%, respectively. Soda PS_1 contains a fraction with particle size above 0.3 mm, whose quantity is 93%. This soda has relatively high values of specific surface area and hygroscopicity (Table 2).

The significant difference of natural soda from synthetic soda in its dispersion, specific surface area, hygroscopicity, and bulk density is related to the specific structure of its particles and the different phase composition, which is corroborated by data of electron microscopy and x-ray phase analysis. Microphotos of soda PS_1, apart from single rod-shaped and rounded crystals, also exhibit strongly bonded conglomerates consisting of mostly discoid crystals forming a packet structure (Fig. 1*a*). The size of single crystals is below 0.25 mm. Microphotos of synthetic soda exhibit loosely bonded conglomerates consisting of discoid and rounded crystals with a clearly expressed pseudo-amorphous surface, which easily disintegrate in shaking and form particles of size below 0.25 mm (Fig. 1*c*).

The phase compositions of synthetic and natural soda were determined by x-ray phase analysis (Fig. 2). It was established that the phase compositions of synthetic and natural soda differ. Thus, the diffraction pattern of raw soda and soda PS_1, apart from reflection maxima corresponding to Na_2CO_3 (d = 2.25 and 2.18), contains reflection maxima corresponding to $Na_2CO_3 \cdot 10H_2O$ (d = 4.50, 3.52, and 2.57), trona $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (d = 3.17, 3.05, and 1.73), and $Na_2SO_4 \cdot 10H_2O$ (d = 5.50 and 4.80), which is related to the conditions of soda layer formation.

The phase composition of soda PS_2 is mostly represented by reflection maxima corresponding to Na_2CO_3 (d = 2.25, 2.18, and 2.70) but, in contrast to synthetic soda, contains reflection maxima corresponding to sodium sulfate (d = 3.84 and 1.84) and sodium hydrocarbonate $NaHCO_3$ (d = 3.04 and 3.49) formed as a consequence of thermal decomposition of trona.

TABLE 1

Soda	Mass content, %						
	Na_2CO_3	Na_2SO_4	NaCl	SiO_2	Al_2O_3	Fe_2O_3	calcination loss
SS	99.01	0.02	0.37	–	–	–	0.60
PS_1	70.00	17.90	0.42	4.71	0.89	0.13	5.95
PS_2	74.47	18.70	0.44	5.10	0.54	0.11	0.64

TABLE 2

Soda	True density, g/cm^3	Specific surface area, cm^2/g	Bulk density, kg/m^3	Hygroscopicity, %
SS	2.83	2920	885.81	58.37
PS_1	2.45	6721	395.78	87.75
PS_2	2.66	4132	848.94	70.46

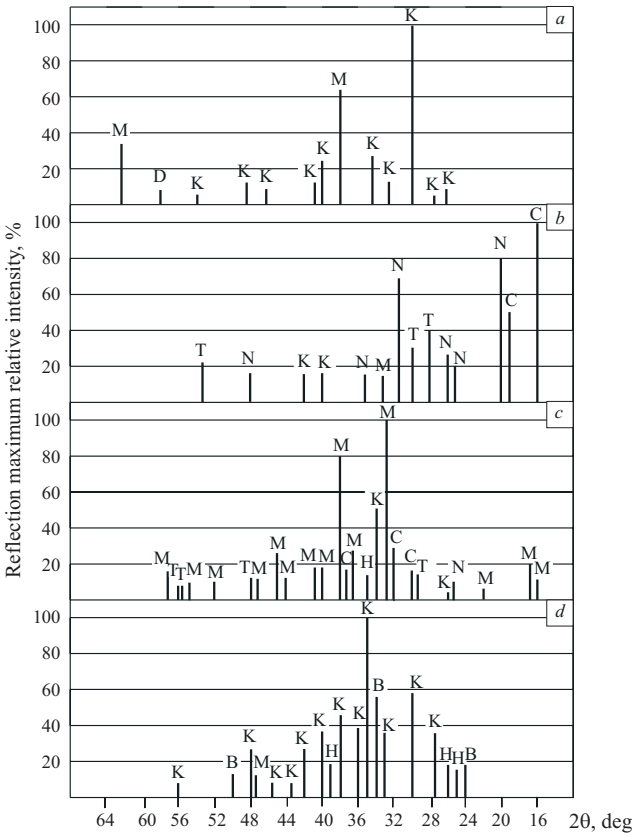

Fig. 2. Diffraction patterns of synthetic soda (*a*), raw soda (*b*), and natural soda dried at room temperatures (*c*) and dried at 350°C (*d*): K) sodium carbonate, M) monohydrate; T) trona, N) natron; C) $Na_2SO_4 \cdot 10H_2O$; H) sodium hydrocarbonate; B) Na_2SO_4; D) $Na_2CO_3 \cdot 2.5H_2O$.

It is known that any method for preparing glass batch implies its moistening, which is accompanied by complex physicochemical processes caused by dissolution and crystallization of components chemically active with respect to water, primarily soda ash. The rate of dissolution and formation of crystal hydrates depends on many factors: size and shape of particles, phase composition, temperature, amount of moisture, moistening method, etc. Evidently, a modification of the alkaline component will affect the phase transformation in the glass batch under moistening.

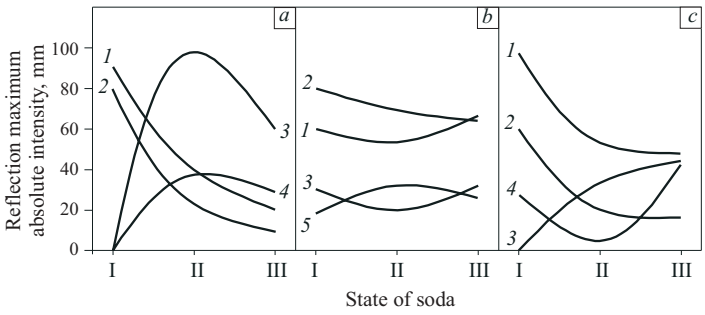

Fig. 3. Variation of phase composition in moistening synthetic soda (*a*), soda PS_1 (*b*), and soda PS_2 (*c*): *1*) $Na_2CO_3 \cdot H_2O$ ($d = 2.37$); *2*) Na_2CO_3 ($d = 2.60$); *3*) $Na_2CO_3 \cdot 10H_2O$ ($d = 2.05$); *4*) $Na_2CO_3 \cdot 2.5H_2O$ ($d = 2.35$); *5*) $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ ($d = 1.65$); I) soda in air-dry state; II and III) soda 2 and 15 min after moistening, respectively.

TABLE 3

Batch	Granule parameters		
	moisture, %	strength, g/granule	yield of standard granules, %
Sh I	26 – 28	600 – 800	65 – 70
Sh II	22 – 24	1000 – 1200	90 – 95

Samples of synthetic and natural soda were investigated 2 and 15 min after moistening using the x-ray phase analysis method. Phase transformations in moistened soda were estimated based on the changes in the intensity of characteristic reflection maxima in time (Fig. 3). It was found that dissolution and crystallization with formation of crystal hydrates $Na_2CO_3 \cdot 10H_2O$ and $Na_2CO_3 \cdot 2.5H_2O$ proceed the most intensely in synthetic soda and in soda PS_2. The less intense processes of dissolution and crystallization in soda PS_1 are probably due to the presence of trona, which delays the formation of high-water crystal hydrates, primarily, natron, which does not contradict published data [3].

Thus, the results of a complex study of properties of natural and synthetic soda indicate a significant difference in their chemical and granulometric compositions and in other physiochemical parameters. The drying conditions of raw soda have a significant effect on the properties of natural soda. Thus, drying at 350°C makes it possible to obtain soda PS_2, which in a number of parameters meets the industrial standard requirements.

In order to investigate the effect of natural soda on the properties of glass batch for sheet glass production at the stage of granulation and melting, an industrial batch was prepared following a previously corrected formula taking into account 50% replacement of synthetic soda by soda PS_2.

Granulation was implemented in a plate granulator with a plate diameter 0.5 m, rotational speed 36 min^{-1}, and plate angle 47°. Premixed batch in the air-dry state was supplied onto a granulator plate moistened with water. The batch was moistened using an injector. The size of standard granules was 10 – 15 mm. Granulation was performed on batch based on synthetic soda (Sh I) and batch with 50% replacement of synthetic soda by soda PS_2 (Sh II).

As a consequence of granulation experiments (Table 3), it was found that introduction of soda PS_2 into a glass batch makes it possible to stabilize the granulation process and increase the yield of standard granules to 90 – 95%. The strength of moist granules in this case grew to 1000 – 1200 g/granule and moisture decreased by 2 – 3%.

Batches for sheet glass production were melted in an electric furnace in corundum crucibles at a temperature of 1450°C with a furnace heating rate of 5 K/min.

The results of experiments performed demonstrated the fundamental possibility of using natural soda for partial replacement of traditional soda-bearing materials in the production of sheet glass and some other types of glass. Despite some difficulties making it necessary to adjust the batch formula and preparation of natural soda, the use of this soda, on the one hand, allows for saving synthetic materials and, on the other hand, contributes to solving environmental problems and complex use of natural raw materials.

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